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VRIJE UNIVERSITEIT
UNIVERSITAT DE GIRONA

Reactivity of Fullerenes, Endohedral Metallofullerenes, and Nanotubes, and
their Possible Application in Solar Energy Conversion

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ter verkrijging van de graad
Doctor aan de Vrije Universiteit Amsterdam,
op gezag van de rector magnificus
prof.dr. V. Subramaniam

en

Doctor in de Exacte Wetenschappen aan de Universitat de Girona
op gezag van de Rector
prof.dr. Sergi Bonet i Marull

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door

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geboren te Matehuala, Mexico

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 dr. Sílvia Osuna Oliveras



Doctoral Thesis:

**Reactivity of Fullerenes, Endohedral Metallofullerenes, and Nanotubes,
and their Possible Application in Solar Energy Conversion**

Juan Pablo Martínez López

May 2017, Doctoral Programme in Chemistry

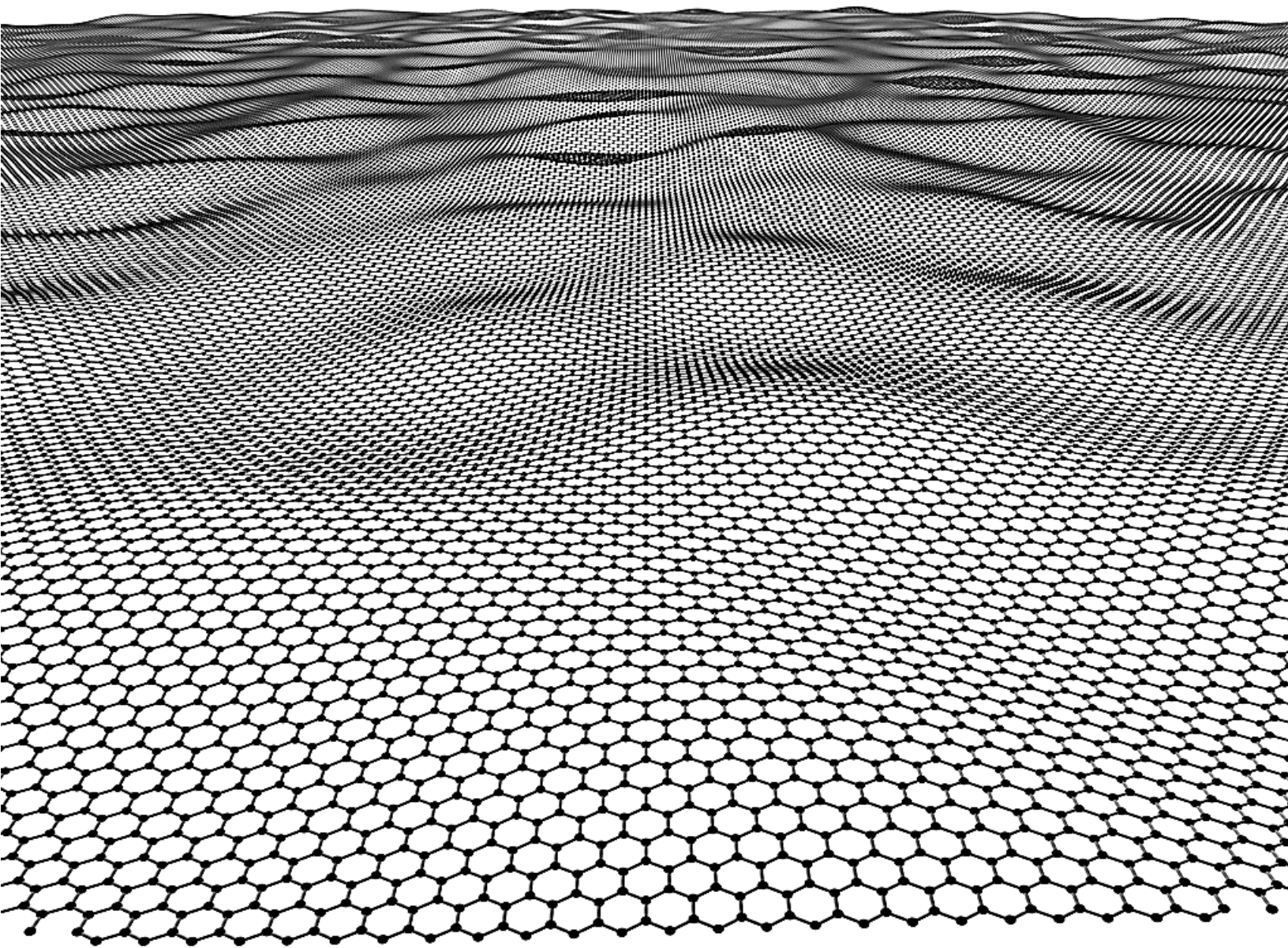
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This manuscript has been presented to jointly opt for the doctoral degree from the
University of Girona and the Free University of Amsterdam



“There’s plenty room at the bottom”

Richard Feynman, December 29th, 1959

Pasadena, California, U.S.A.

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Juan Pablo Mtz., spring 2017

List of Publications

This Thesis is presented as a compendium of publications.

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1. Martínez, J.P.; Osuna, S.; Solà, M.; Voityuk, A., “Extent of Charge Separation and Exciton Delocalization for Electronically Excited States in a Triphenylamine- C_{60} Donor-Acceptor Conjugate: a Combined Molecular Dynamics and TD-DFT Study”, *Theor. Chem. Acc.* **2015**, 134, 12. (Impact Factor 1.806, 3rd quartile)
2. Martínez, J.P.; Solà, M.; Poater, A., “On the Reaction Mechanism of the Rhodium-Catalyzed Arylation of Fullerene (C_{60}) with Organoboron Compounds in the Presence of Water”, *ChemistryOpen* **2015**, 4, 774-778. (Impact Factor 3.585, classified as *Very Important Paper* by the editors, 2nd quartile)
3. Martínez, J.P.; Langa, F.; Bickelhaupt, F.M.; Osuna, S.; Solà, M., “(4+2) and (2+2) Cycloadditions of Benzyne to C_{60} and Zig-Zag Single-Walled Carbon Nanotubes: The Effect of the Curvature”, *J. Phys. Chem. C* **2016**, 120, 1716-1726. (Impact Factor 4.509, 1st quartile)
4. Martínez, J.P.; Garcia-Borràs, M.; Osuna, S.; Poater, J.; Bickelhaupt, F.M.; Solà, M., “Reaction Mechanism and Regioselectivity of the Bingel-Hirsch Addition of Dimethyl Bromomalonate to $La@C_{2v}-C_{82}$ ”, *Chem. Eur. J.* **2016**, 22, 5953-5962. (Impact Factor 5.771, 1st quartile)
5. Martínez, J.P.; Solà, M.; Voityuk, A.A., “Theoretical Estimation of the Rate of Photoinduced Charge Transfer Reactions in Triphenylamine C_{60} Donor-Acceptor Conjugate”, *J. Comput. Chem.* **2016**, 37, 1396-1405. (Impact Factor 3.648, 1st quartile)
6. Martínez, J.P.; Vummaleti, S.V.C.; Falivene, L.; Nolan, S.P.; Cavallo, L.; Solà, M.; Poater, A., “In Silico Olefin Metathesis with Ru-based Catalysts Containing N-Heterocyclic Carbenes Bearing C_{60} Fullerenes”, *Chem. Eur. J.* **2016**, 22, 6617-6623. (Impact Factor 5.771, 1st quartile)

List of Abbreviations

Abbreviation	Description
ASM	Activation Strain Model
BC	Benzyne Cycloaddition
BH	Bingel-Hirsch
cod	1,5-cyclooctadiene
COSMO	COnductor-like Screening MOdel
CR	Charge Recombination
CS	Charge Separation
CT	Charge Transfer
CTS	Charge Transfer State
DFT	Density Functional Theory
dmbm⁻	DiMethyl BromoMalonate anion
ΔG_{cr}	Gibbs energy of a charge recombination reaction
ΔG_{cs}	Gibbs energy of a charge separation reaction
ΔG_{ct}	Gibbs energy of a photoinduced charge transfer reaction
DSSC	Dye-Sensitized Solar Cell
EMF	Endohedral MetalloFullerene
ET	Electron Transfer
HF	Hartree-Fock
HOMO	Highest Occupied Molecular Orbital
HS	Hybrid State
IPR	Isolated Pentagon Rule
IR	InfraRed
k_{cr}	Rate constant of a charge recombination reaction
k_{cs}	Rate constant of a charge separation reaction
k_{ct}	Rate constant of a photoinduced charge transfer reaction
λ	Total reorganization energy
λ_{ext}	Outer-sphere or external reorganization energy
λ_{int}	Inner-sphere or internal reorganization energy
LES	Localized Excited State
LR	Linear Response
LUMO	Lowest Unoccupied Molecular Orbital
μ	Molecular dipole moment
MD	Molecular Dynamics
MO	Molecular Orbital
MR	Membered Ring; it is indeed denoted as x -MR ($x = 3, 4, 5$, or 6)
NHC	N-Heterocyclic Carbene
NMR	Nuclear Magnetic Resonance
ω	Frequency, time

PES	Potential Energy Surface
SIMes	1,3-bis[2,4,6-(trimethyl)phenyl]imidazolidin-2-ylidene
SWCNT	Single-Walled Carbon NanoTube
TD	Time Dependent
TD-DFT	Time-Dependent Density Functional Theory
TNT	Trimetallic Nitride Template
TPA	TriPhenylAmine
TS	Transition State
UV-vis	UltraViolet-visible
$v_{ext}(\mathbf{r})$	External potential
V_{ij}	Electronic coupling

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Summary of the Thesis

Carbon is able to form several allotropes with interesting medical, scientific, and industrial applications, among others. Particularly, fullerenes and carbon nanotubes have attracted the attention of many scientific research groups through the entire world since they were discovered by Kroto, Smalley, and Curl in 1985, and by Sumio Iijima in 1991, respectively. The understanding of chemical and physical properties of these carbon nanostructures is crucial for the development of applications such as the synthesis of biomarkers, construction of efficient organic photovoltaic devices, and design of materials with increased resistance to thermal deformation, chemical corrosion, and mechanical stress; among others. Accordingly, this thesis is aimed at the comprehensive, quantum-computational description of the chemical functionalization and charge transfer events susceptible to take place at (endohedral)fullerenes and carbon nanotubes; thus providing a systematic understanding of experimentally reported phenomena.

The current manuscript contains a series of seven chapters distributed according to a compendium of publications. In Chapter 1, molecular structures and chemical functionalization of (endohedral)fullerenes and nanotubes are reviewed. In chapter 2, a revision of quantum-based theories, as well as methodologies used in the thesis, and the electron transfer problem is also introduced. In Chapter 3 the goals to reach in each one of the research projects included in this thesis are established; these latter ones are reported as a sequence of publications in chapters 4, 5, and 6.

Chapter 4 develops the study of cycloaddition reactions to carbon nanostructures. The main subject of study is the chemo- and regioselectivity of the Bingel-Hirsch addition of dimethyl bromomalonate to the endohedral metallofullerene $\text{La}@C_{2v}\text{-C}_{82}$; a special case study because of the paramagnetic nature and the many nonequivalent carbon atoms in the cage. Then, the (2+2) and (4+2) cycloadditions of benzyne to fullerene C_{60} and a series of zig-zag single-walled carbon nanotubes differing in diameter is analyzed in detail so as to account for the experimentally observed changes in reactivity; that is to say, (2+2) and (4+2) cycloadditions shall depend on the diameter and chirality of the carbon nanostructure.

The potential applications of fullerene C_{60} in chemical reactions catalyzed by transition metal complexes are discussed in Chapter 5. The first study consists in the quantum-based development of a Suzuki-Miyaura-like reaction mechanism for the arylation of C_{60} with organoboron compounds catalyzed by a rhodium complex in the presence of water, which leads to an arylated hydrofullerene. After that, the catalytic capability of a ruthenium complex, which is linked to N-heterocyclic carbenes containing C_{60} , is analyzed for olefin metathesis (ethylene in this study), wherein it is demonstrated that the inclusion of C_{60} in ruthenium-based catalysts improves the catalytic power.

In Chapter 6, charge transfer events are studied for a fullerene dye-sensitized solar cell, the triphenylamine-C₆₀ donor-acceptor conjugate is taken as the reference system. Excitons with neutral, strong charge transfer, and even with partial charge transfer character are carefully described so as to determine nonadiabatic rates of photoinduced charge transfer reactions in such materials. The proper estimation of electron transfer parameters from a quantum-theoretical framework strongly influences the design of higher-efficient light-harvesting photovoltaic devices.

In Chapter 7, the most relevant results of the former chapters are summarized following the sequence of chapters 4-6. Finally, in Chapter 8, the main goals achieved in the current research work are highlighted for the chemical functionalization of carbon nanostructures and their potential application in solar energy conversion.

Samenvatting Proefschrift

Koolstof komt voor in verscheidene allotropen die elk interessante medische, wetenschappelijke en industriële toepassingen hebben. Met name de door Kroto, Smalley en Curl (1985) respectievelijk Sumio Iijima (1991) ontdekte fullerenen en koolstof nanobuisjes hebben wereldwijd de aandacht van veel onderzoeksgroepen getrokken. Het begrijpen van de chemische en fysische eigenschappen van deze koolstof nanostructuren is cruciaal voor de ontwikkeling van toepassingen zoals de synthese van biomarkers, de constructie van efficiënte organische zonnecellen en de ontwikkeling van materiaal met verhoogde weerstand tegen thermische vervorming, chemische corrosie en mechanische belasting. Hiervan uitgaande richt dit proefschrift zich op de uitgebreide, quantumcomputationele beschrijving van de chemische functionalisering van (endohedrale) fullerenen en koolstof nanobuisjes en ladingsoverdrachtsprocessen die in deze verbindingen kunnen plaatsvinden. Door het hier beschreven systematische onderzoek wordt een beter inzicht verkregen van de betekenis van eerder behaalde maar voorheen onvolledig begrepen experimentele gegevens.

Het onderhavige manuscript omvat zeven hoofdstukken. In hoofdstuk 1 worden moleculaire structuren en de chemische functionalisering van (endohedrale) fullerenen en nanobuisjes besproken. In hoofdstuk 2 wordt een overzicht gepresenteerd van op de quantummechanica gebaseerde theorieën evenals van rekenmethoden die worden gebruikt in het proefschrift. Tevens wordt het elektronen-overdrachtsprobleem geïntroduceerd. Hoofdstuk 3 geeft een overzicht van de doelstellingen van de verschillende deelprojecten die vervolgens in de hoofdstukken 4, 5 en 6 besproken worden. Deze resultaten zijn eveneens in de vorm van publicaties in wetenschappelijke tijdschriften verschenen.

Hoofdstuk 4 behandelt de studie van de cycloadditie reacties op koolstof nanostructuren. Het belangrijkste onderwerp van deze studie is de chemo- en regio-selectiviteit van de Bingel-Hirsch-additie van dimethylbroommalonaat aan endohedrale metallofullerenen $\text{La}@C_{2v}\text{-C}_{82}$. Dit is een speciale casestudie, vanwege de para-magnetische natuur en het grote aantal niet-equivalente koolstofatomen in de kooi. Vervolgens worden de (2+2) en (4+2) cycloaddities onderzocht van benzyn aan het fullereen C_{60} alsmede aan een reeks zig-zag single-walled koolstof nanobuisjes die in diameter verschillen. Deze gedetailleerde analyses dienen een beter begrip van de experimenteel waargenomen veranderingen in de reactiviteit van de (2+2) en (4+2) cycloaddities als functie van de diameter en de chiraliteit van de koolstof nanostructuur.

Hoofdstuk 5 behandelt de mogelijke toepassingen van het fullereen C_{60} bij door overgangsmetaalcomplexen gekatalyseerde chemische reacties. De eerste studie omvat de quantum-gebaseerde ontwikkeling van een Suzuki-Miyaura-achtig reactie-mechanisme voor de arylering van C_{60} met behulp van organoboorverbindingen. Deze reactie wordt in de aanwezigheid van water gekatalyseerd door een rhodium complex en leidt tot een gearyleerd

hydrofullereen. Vervolgens wordt het katalytische vermogen geanalyseerd van een ruthenium complex bij de metathese van alkenen, in dit geval etheen. Het betreffende ruthenium complex is gekoppeld aan N-heterocyclische carbenen met een C₆₀-groep. Hierbij wordt aangetoond dat de C₆₀-groepen een verbetering van het katalytisch vermogen teweegbrengen.

In Hoofdstuk 6 worden ladingsoverdrachtsprocessen voor een fullereen kleurstof-ge sensibiliseerde zonnecel bestudeerd, waarbij het trifenylamine-C₆₀ donor-acceptor conjugaat als referentiesysteem dient. Niet-adiabatische snelheden van foto-geïnduceerde ladingsoverdrachtsreacties worden bepaald door middel van een nauwkeurige beschrijving van excitonen met uiteenlopend ladingsoverdrachtskarakter (dat wil zeggen: geen, partieel, sterk). De juiste inschatting van elektronenoverdrachtsparameters op basis van quantumchemische berekeningen leidt tot een doelgericht ontwerp van efficiëntere zonnecellen.

Hoofdstuk 7 geeft een samenvatting van de resultaten uit de drie voorgaande hoofdstukken. Tenslotte richt zich hoofdstuk 8 op de hoofddoelen die in dit onderzoek bereikt zijn en werkt de hoogtepunten uit met betrekking tot de chemische functionalisering van koolstof nanostructuren en hun toepassingsmogelijkheden in de winning en omzetting van energie uit zonlicht.

Resum de la Tesi

L'element de carboni és capaç de formar diversos al·lòtrops amb interessants aplicacions mèdiques, científiques i industrials, entre altres. En concret, els ful·lerens i nanotubs de carboni han atret l'atenció de molts grups d'investigació científica de tot el món des que van ser descoberts per Kroto, Smalley i Curl el 1985, i per Sumio Iijima el 1991, respectivament. La comprensió de les propietats químiques i físiques d'aquestes nanoestructures de carboni és crucial per desenvolupar aplicacions com la síntesi de biomarcadors, la construcció d'eficients dispositius fotovoltaics orgànics, i el disseny de materials amb alta resistència a la deformació tèrmica, la corrosió química, i a l'estrès mecànic; entre altres. D'acord amb això, mitjançant modelatge quàntic computacional, aquesta tesi està enfocada a la descripció detallada de la funcionalització química i esdeveniments de transferència de càrrega susceptibles d'ocórrer en els ful·lerens (endoèdrics) i nanotubs de carboni; proporcionant així un enteniment sistemàtic dels fenòmens observats experimentalment.

El present manuscrit conté una sèrie de set capítols distribuïts segons un compendi de publicacions. En el Capítol 1, es presenten les estructures moleculars i la funcionalització química dels ful·lerens (endoèdrics) i nanotubs de carboni. En el Capítol 2, es revisen les teories basades en mecànica quàntica, així com les metodologies utilitzades en aquesta tesi, i el problema de la transferència d'electrons. En el Capítol 3 s'estableixen els objectius a assolir en cada un dels projectes de recerca inclosos en aquesta tesi; aquests últims es presenten com una seqüència de publicacions dins dels capítols 4, 5 i 6.

En el Capítol 4 es desenvolupa un estudi sobre reaccions de cicloadició a nanoestructures de carboni. L'objectiu principal d'estudi és la químic i regioselectivitat de l'addició Bingel-Hirsch del dimetil bromomalonat al metal·loful·lerene endoèdric $\text{La}@C_{2v}\text{-C}_{82}$; un cas especial a causa de la seva naturalesa paramagnètica i dels molts àtoms de carboni no equivalents en l'estructura. Subseqüentment, les cicloadicions (2+2) i (4+2) del benzí al ful·lerè C_{60} i diversos nanotubs de carboni de paret simple tipus zig-zag de diferent diàmetre s'analitzen en detall per tal d'explicar els canvis en la reactivitat observats experimentalment; és a dir, les cicloadicions (2+2) i (4+2) dependran del diàmetre i de la quiralitat de la nanoestructura de carboni.

Les aplicacions potencials del ful·lerè C_{60} en reaccions químiques catalitzades per complexos de metalls de transició es discuteixen en el Capítol 5. El primer estudi consisteix en el desenvolupament, fonamentat en metodologia quàntica, d'un mecanisme de reacció tipus Suzuki-Miyaura per a l'arilació de C_{60} amb organoborats, la qual és catalitzada per un complex de rodi en presència d'aigua, que condueix a un hidroful·lerè arilat. Després d'això, la capacitat catalítica d'un complex de ruteni, el qual té com a lligands carbens N-heterocíclics contenant C_{60} , s'analitza per a la metàtesi d'olefines (etilè en aquest estudi), del qual es demostra que la inclusió de C_{60} en catalitzadors basats en ruteni millora el seu poder catalític.

En el Capítol 6 s'estudien els processos de transferència de càrrega per a una cèl·lula solar sensibilitzada per colorant a base de ful·lerè, sent la trifenilamina- C_{60} el conjugat donant-acceptor de referència. Els excitons amb caràcter neutre, amb forta transferència de càrrega, i amb caràcter parcial de transferència de càrrega es descriuen acuradament per tal de determinar les velocitats no adiabàtiques de reaccions de transferència de càrrega fotoinduídes en aquests materials. L'estimació correcta dels paràmetres de transferència d'electrons a partir d'un marc teòric quàntic influeix significativament en el disseny de dispositius fotovoltaics de captació de llum amb una major eficiència.

En el Capítol 7, es resumeixen els resultats més rellevants seguint la seqüència dels capítols 4-6. Finalment, en el Capítol 8, es destaquen les principals fites assolides en el present treball de recerca per a la funcionalització química de nanoestructures de carboni i llurs potencials aplicacions en la conversió d'energia solar.

Resumen de la Tesis

El elemento de carbono es capaz de formar varios alótropos con interesantes aplicaciones médicas, científicas e industriales, entre otras. En particular, los fullerenos y nanotubos de carbono han atraído la atención de muchos grupos de investigación científica a través de todo el mundo desde que fueron descubiertos por Kroto, Smalley y Curl en 1985, y por Sumio Iijima en 1991, respectivamente. La comprensión de las propiedades químicas y físicas de estas nanoestructuras de carbono es crucial para desarrollar aplicaciones como la síntesis de biomarcadores, la construcción de eficientes dispositivos fotovoltaicos orgánicos, y el diseño de materiales con alta resistencia a la deformación térmica, la corrosión química, y al estrés mecánico; entre otras. De acuerdo con ello, mediante modelado cuántico computacional, esta tesis está enfocada a la descripción detallada de la funcionalización química y eventos de transferencia de carga susceptibles de ocurrir en los fullerenos (endoédricos) y nanotubos de carbono; proporcionando así un entendimiento sistemático de los fenómenos observados experimentalmente.

El presente manuscrito contiene una serie de siete capítulos distribuidos según un compendio de publicaciones. En el Capítulo 1, se revisan las estructuras moleculares y la funcionalización química de fullerenos (endoédricos) y nanotubos de carbono. En el Capítulo 2, se introduce una revisión de las teorías basadas en mecánica cuántica, así como las metodologías utilizadas en esta tesis, y el problema de la transferencia de electrones. En el Capítulo 3 se establecen los objetivos a alcanzar en cada uno de los proyectos de investigación incluidos en esta tesis; éstos últimos se presentan como una secuencia de publicaciones dentro de los capítulos 4, 5 y 6.

En el Capítulo 4 se desarrolla un estudio sobre reacciones de cicloadición en nanoestructuras de carbono. El objetivo principal de estudio es la quimio y regio-selectividad de la adición Bingel-Hirsch de dimetil bromomalonato en el metalofullereno endoédrico $\text{La}@C_{2v}\text{-C}_{82}$; un caso especial debido a la naturaleza paramagnética y a los muchos átomos de carbono no equivalentes en la estructura. Subsecuentemente, las cicloadiciones (2+2) y (4+2) de bencino en el fullereno C_{60} y en varios nanotubos de carbono de pared simple tipo zig-zag de diferente diámetro son analizadas en detalle con el fin de explicar los cambios en la reactividad observados experimentalmente; es decir, las cicloadiciones (2+2) y (4+2) dependerán del diámetro y de la quiralidad de la nanoestructura de carbono.

Las aplicaciones potenciales del fullereno C_{60} en las reacciones químicas catalizadas por complejos de metales de transición se discuten en el Capítulo 5. El primer estudio consiste en el desarrollo, fundamentado en metodología cuántica, de un mecanismo de reacción tipo Suzuki-Miyaura para la arilación de C_{60} con organoboratos catalizada por un complejo de rodio en presencia de agua, lo que conduce a un hidrof fullereno arilado. Después de eso, la capacidad catalítica de un complejo de rutenio, que tiene como ligandos a carbenos N-heterocíclicos conteniendo C_{60} , se analiza para la metátesis de olefinas (etileno en este

estudio), del cual se demuestra que la inclusión de C_{60} en catalizadores a base de rutenio mejora el poder catalítico.

En el Capítulo 6 se estudian los eventos de transferencia de carga para una célula solar sensibilizada por colorante a base de fullereno, siendo la trifenilamina- C_{60} el conjugado donante-aceptor de referencia. Excitones con carácter neutro, con fuerte transferencia de carga, e incluso con carácter parcial de transferencia de carga se describen cuidadosamente con el fin de determinar las velocidades no adiabáticas de reacciones de transferencia de carga fotoinducidas en dichos materiales. La estimación correcta de los parámetros de transferencia de electrones a partir de un marco teórico cuántico influye significativamente en el diseño de dispositivos fotovoltaicos de captación de luz con una mayor eficiencia.

En el Capítulo 7, los resultados más relevantes son resumidos siguiendo la secuencia de los capítulos 4-6. Por último, en el Capítulo 8, se destacan las principales metas alcanzadas en el presente trabajo de investigación para la funcionalización química de nanoestructuras de carbono y su potencial aplicación en la conversión de energía solar.